The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1984 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Intramolecular dephasing in pyrazine: Direct picosecond time resolution

J. L. Knee, F. E. Doany, and A. H. Zewail[a)]
Arthur Amos Noyes Laboratory of Chemical Physics,[b)] California Institute of Technology, Pasadena, California 91125

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Because of its importance to the theory of radiationless transitions in isolated molecules, the problem of intramolecular dephasing and relaxation in pyrazine is perhaps the most studied case so far. In this molecule, a singlet state rovibronic level (JK) is coupled to a set of rovibronic triplet manifold of levels, computed to be approximately 13 in number.[1] Because of this coupling (so-called intermediate coupling case) the fluorescence[2] is expected to exhibit a *biexponential* decay[3] together with some complicated *quantum beats*. The fast component of the decay is due to the coherent dephasing of molecular eigenstates (ME's), which are excited coherently by the light source and interfere during the decay to give beats. The slow decay component, on the other hand, simply gives the (average) lifetime of these ME's.

The slow component and the quantum beats have been characterized experimentally by time- and frequency-resolved spectroscopy,[4–8] and by magnetic field studies.[6,7] The origin of the fast component ($\sim$150 ps), however, has been questioned by Kommandeur's group.[9] Based on high-resolution studies of ME's, Kommandeur *et al.*[9] ascribed the fast component as due to a Rayleigh-type scattering and not to the intrinsic molecular dephasing expected in this case. Earlier time-resolved experiments have shown that this fast component is about 150 ps in duration,[6,8] and more recent work by Rice's group[10] has shown that careful deconvolution of the fluorescence transient with the response function of their apparatus (100 ps) yielded a molecular decay of 103 ps.

It is the purpose of this Communication to report on the direct observation of this fast component with a time resolution limited only by our pulse (2 or 10 ps). To achieve this temporal resolution we used picosecond pulses in a pump–probe configuration. The experiments were performed on jet-cooled pyrazine in a skimmed molecular beam apparatus. The results presented here prove that the fast component is *not* Rayleigh-type scattering and it is due to a *molecular* dephasing process.

The laser system consists of a (DCM) dye laser, synchronously pumped by a mode locked Ar^+ laser and amplified in three stages using the second harmonic of a Nd^{+3} YAG laser. Typical pulse widths were 2 ps but using a three plate birefringent tuning element yielded pulses with $\sim$10 ps duration and $\sim$1 Å bandwidth. The amplified pulse energy was typically 0.5–0.75 mJ/pulse.

Devising a pump–probe photoionization scheme for pyrazine in the supersonic beam[11] is difficult because S_1(30 876 cm^{-1}) is much less than halfway to the ionization potential ($\sim$79 050 cm^{-1}). Thus the method previously used for stilbene,[11] namely one UV photon as the pump and two-visible photons as the probe, cannot be used for pyrazine. To obtain pyrazine transients we have probed with two photons at 4026 Å. This wavelength was generated by mixing the amplified 6477 Å pulses with the fundamental of the amplifying YAG (1.06 μm) in a Type II KD*P crystal. The conversion efficiency was $\sim$15%.

The UV pump (6477/2 Å) and blue probe (4026 Å) were focused into the supersonic beam 12 cm downstream from the nozzle and 9 cm from the skimmer (1.3 mm), Fig. 1. The backing pressure was 30 psi (He) and the detection chamber pressure was 1×10^{-6} Torr. The product ions were mass resolved in a TOF mass spectrometer.

The ionization signal, when both beams were overlapped in time and space, gave an enhancement of greater than ten times the UV alone signal. Data acquisition was as previously reported.[11,12]

Data was taken by delaying the blue pulse relative to the

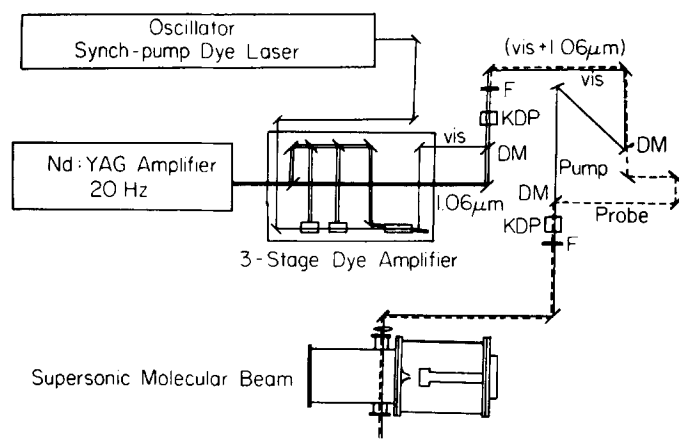

FIG. 1. Schematic diagram for picosecond pump–probe experiments done on pyrazine in a supersonic molecular beam. The abbreviations are as follows: KDP potassium dihydrogen phosphate crystal; F filter; DM dichroic mirror.

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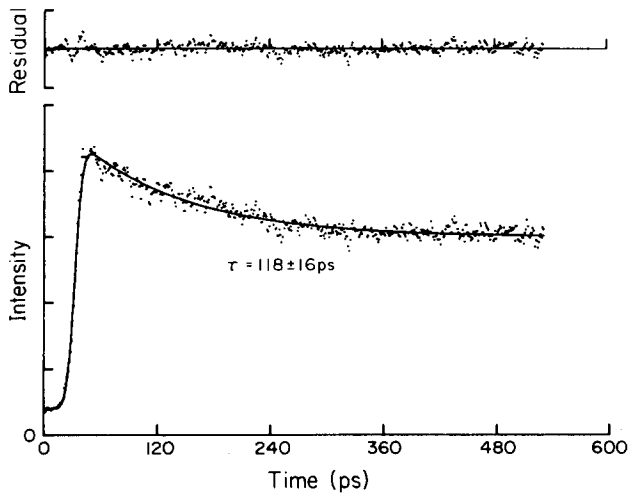

FIG. 2. Observed probe signal intensity as a function of (pump–probe) delay time for the pyrazine origin. The pump wave length is 3238.5 Å and the probe is two photons at 4026 Å (see the text). The solid line through the data is the computed best fit which yields a decay time constant of 118 ± 16 ps. Note that the ratio of the fast/slow decay components is determined by the efficiency of ionization by the probe pulse and comparison with fluorescence ratio requires details of the kinetics (Ref. 14). Pyrazine was seeded in pure He at a packing pressure of 30 psi.

UV pulse over a range of 532 ps. The fast exponential at the pyrazine origin (30 876 cm^{-1}) is 118 ± 16 ps. The slow exponential, which is known to be on the microsecond time scale, is flat over our time period. The decay curve with computed best fit is shown in Fig. 2.

From the data presented here it is evident that the fast component does not follow the response of our short pulse. Instead, we observe a decay component of 118 ps after the pulse is turned *off*. This indicates that the decay is not Rayleigh-type scattering and it is indeed *molecular* in nature. Furthermore, the result also removes the doubt[9] that a Rayleigh wing can be responsible for observations made by pulses (or detection responses) with duration comparable to the dephasing time, i.e., the 118 ps. A reexamination of the nature of ME's[1] is now needed.[13] A full account of our picosecond work will be published later when we complete work on deutropyrazine and other azines.

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Laser spectroscopy of organometallic free radicals

C. R. Brazier, P. F. Bernath, S. Kinsey-Nielsen, and L. C. Ellingboe
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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We have observed more than a dozen new organometallic free radicals. Calcium and strontium have been found to react in the gas phase with a wide variety of organic molecules including aldehydes, ketones, alcohols, and carboxylic acids. The reaction products are free radical metal salts with electronic states closely related to the alkaline earth monohalides. The reactions occur with ground state reagents, however, an enhancement of more than three orders of magnitude in the concentration of products was observed using laser excitation of the metal atoms.

The first new molecule was observed when acetone was inadvertently introduced into a Broida oven[1] containing Sr vapor. In such a system, metal atoms are evaporated from a resistively heated crucible, entrained in an argon carrier gas and then allowed to react with a suitable oxidant.[1] Figure 1 shows a laser excitation spectrum of the Sr plus acetone reaction obtained by scanning a broad band (1 cm^{-1}) cw dye laser and detecting the total fluorescence. The Q heads of SrOH $A\,^2\Pi_{1/2}$–$X\,^2\Sigma^+$ appear[2–3] near the Sr atomic line ($^3P_1$–$^1S_0$) and 270 cm^{-1} to the blue are the $A\,^2\Pi_{3/2}$–$X\,^2\Sigma^+$ Q heads.

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